OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT N00014-88-K-0007

R&T CODE 4132020

TITLE: STRUCTURE-PROPERTY BEHAVIOR OF NEW ORGANIC-INORGANIC POLYMERIC HYBRID MATERIALS BASED ON SOL GEL CHEMISTRY

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May 1990

Part I

a&b) Papers Published/Submitted to Refereed Journals:

1) G.L. Wilkes, B. Wang, A.B. Brennan, D. Rodrigues and H.H. Huang, "New Hybrid Inorganic-Organic Materials Made by the Sol-Gel Method: Synthesis, Structure-Property Behavior," Materials Research Symposium, Polymer-Based Molecular Composites, Nov. 1989.

2) B. Wang, H.H. Huang, A.B. Brennan and G.L. Wilkes, "Synthesis and Characterization of New Alumina Containing Organic/Inorganic Hybrid Materials from Sol-Gel Processing," Polymer Preprints, 30(2), (1989).

3) B. Wang, A.B. Brennan, H.H. Huang and G.L. Wilkes, "Synthesis and Characterization of New Alumina and Titania Containing Hybrid Materials from Sol-Gel Processing," J. Macromol. Sci.-Chem., submitted.

4) B. Wang and G.L. Wilkes, "New Ti-PTMO and Zr-PTMO Ceramics Hybrid Materials Prepared by the Sol Gel Method: Synthesis and Characterization," J. Polym. Sci., Polym. Letters, submitted.

5) B. Wang, H. Huang, G.L. Wilkes, S.C. Liptak and J.E. McGrath, "New High Refractive Index Organic/Inorganic Hybrid Materials from Titanium Tetraisopropoxide and Functionalized Poly(Arylene Ether Sulfone) Prepared by the Sol Gel Process," Polym. Materials Sci. Engr., 63, (1990) in press.

6) A.B. Brennan, H.H. Huang and G.L. Wilkes, "Structure-Property Behavior of Sol-Gel Derived Hybrid Materials - Effect of Polymeric Acid Catalyst," Polym. Preprints, 30(2) (1989).

7) H.H. Huang, R.H. Glaser, A.B. Brennan, D.E. Rodrigues and G.L. Wilkes, "Structure-Property Study of Hybrid Materials Incorporating Organic Oligomers into Sol-Gel Systems," Symposium on Ultrastructure Processing of Materials, Tucson, 1989, in press.

8) A.B. Brennan and G.L. Wilkes, "Structure-Property Behavior of Sol-Gel Derived Hybrid Materials - Effect of Polymeric Acid Catalyst, accepted for publication in Polymer.

9) M. Spinu, A.B. Brennan, G.L. Wilkes and J.E. McGrath, "Poly(arylene ether) or Polyimide-Silicate Hybrids Via Sol-Gel Ultrastructure Processing," Materials Research Symposium, Polymer-Based Molecular Composites, Nov. 1989.

10) D.E. Rodrigues and G.L. Wilkes, "Structure-Property Behavior of Sol-Gel Derived Hybrid Ceramer Materials Using Microwave Processing," Polymer Preprints, 32(2) (1989).

11) D.E. Rodrigues and G.L. Wilkes, "Features of Microwave Processing of Inorganic/Organic Hybrid Networks (Ceramic) Materials," MRS, San Francisco in Microwave Symposia, April 1990, submitted.

c-g) N/A

h) Invited Presentations at Topical or Scientific/Technical Society Conferences

h1) David Rodrigues and Garth L. Wilkes, "Synthesis/Structure Properties of New Ceramer Hybrid Organic/Inorganic Networks Prepared by a Sol-Gel Process - New Developments in Processing by Utilizing Microwave Processing, invited paper, MRS Meeting, San Francisco, Califronia, April 1990.

h2) Garth L. Wikes, "Inorganic/Organic Hybrid Networks," Gordon Conference on Thermoset Polymers, July 1989, New London, New Hampshire.

h3) G.L. Wilkes, B. Wang, A.B. Brennan, D.E. Rodrigues and H.H. Huang, "New Hybrid Inorganic-Organic Materials Made by the Sol Gel Method - Synthesis, Structure/Property Behavior," Invited Paper, Materials Research Symposium, Polymer Based Molecular Composites, Boston, MA, November 1989.

i) Contributed Presentations at Topical or Scientific/Technical Society Conference

i1) A.B. Brennan, H.H. Huang and G.L. Wilkes, "Structure-Property Behavior of Sol-Gel Derived Hybrid Materials - Effect of Polymeric Acid Catalyst," American Chemical Society, 198th National Meeting, Miami Beach, FL, September 1989.

i2) A.B. Brennan, H.H. Huang and G.L. Wilkes, "Structure-Property Behavior of New Hybrid Materials Incorporating Poly(tetramethylene Oxide) with Inorganic Silicates by Sol Gel Processing," Southeastern Graduate Polymer Conference, Georgia Institute of Technology, Atlanta, GA, April 1989.

i3) A.B. Brennan, "Sol Gel Chemistry - A Novel Route to Hybrid Materials," Center for Adhesives and Sealant Science, Virginia Polytechnic Institute & State University, April 3, 1990.

i4) A.B. Brennan, H.H. Huang and G.L. Wilkes, "Structure-Property Behavior of Sol-Gel Derived Hybrid Materials - Effect of Polymeric Acid Catalyst," Conference on Polymeric Materials and Interfaces, Blacskburg, VA, October 1989.

i5) B. Wang, A.B. Brennan, H.H. Huang and G.L. Wilkes, "Synthesis and Characterization of New Titania and Zirconia Containing Hybrid Materials from Sol-Gel Processing," Conference on Polymeric Materials and Interfaces, Blacksburg, VA, October 1989.

i6) D.E. Rodrigues and G.L. Wilkes, "Features of Microwave Processing of Inorganic/Organic Hybrid Networks (Ceramic) Materials," MRS Symposia, San Francisco, CA, April 1990.

i7) D.E. Rodrigues and G.L. Wilkes, "Structure-Property Behavior of Sol Gel Derived Hybrid Ceramer Materials Using Microwave Processing," American Chemical Society, 198th National Meeting, Miami Beach, FL, September 1989.

i8) B. Wang, H.H. Huang, A.B. Brennan and G.L. Wilkes, "Synthesis and Characterization of New Alumina Containing Organic/Inorganic Hybrid Materials," American Chemical Society, 198th National Meeting, Miami Beach, FL, September 1989.

j) N/A

k) Number of graduate students receiving full or partial support - two

l) Number of Post Doctoral fellows receiving full or partial support - one

m) N/A

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PART II

a) Principal Investigator: Garth L. Wilkes

b) Current Telephone Number: (703) 231-5498

c) Cognizant ONR Scientific Officer
Dr. Kenneth J. Wynne

d) *Brief Description of Project:*

The purpose of this work has been to synthesize and characterize the structure-property response of new inorganic-organic hybrid materials that incorporate functionalized organic oligomers with metal alkoxides through the use of sol gel reactions. These systems, which have been termed "ceramers" as a result of their possessing properties of both ceramic like materials (inorganic glasses) as well as organic polymers, can vary significantly in their properties due to altering the amount of respective metal alkoxide species relative to the functionalized organic components which may be oligomeric or even of lower molecular weight. The hope is this approach will lead to new hybrid network materials with unique properties. In many instances, the characterization of these materials as well as some of their mechanical, optical and electronic properties have been investigated.

e) Significant Results During Last Year

Considerable progress has been made in terms of the synthesis of several new ceramer materials possessing unique properties - particularly high refractive index coating materials. Many of our investigations have focused on using lower Tg (elastomeric) organic oligomers that are functionalized and which after reacting with metal alkoxides, leads to more rubberlike materials. However, more recently we have emphasized developing ceramers using high Tg oligomers. Specific examples include polyarylene ether sulfones, polyarylene ether ketones and more recently progress has been made even utilizing high Tg polyimide oligomers. The majority of these systems have been developed into network ceramers utilizing a variety of metal alkoxides based on either silicon, aluminum, titanium or zirconium. In the specific case of the titanium based materials, extremely high refractive index transparent materials have been achieved possessing refractive index values high above the common high refractive index organic polymers that are known. Due to incorporation of the organic, its presence provides significant flexibility to these final materials and hence potential of such systems for optical coatings or encapsulant applications seems significant. In addition, these materials have also displayed reasonable dielectric properties in view of their composition. Further structural characterization of the ceramer materials utilizing the techniques of solid state NMR, small angle x-ray scattering as well as electron microscopy have continued and have shed additional light on the morphological features of these systems. We have developed further control of that morphological texture by utilizing different reaction conditions that will promote variation in the level of microphase separation which influences final property response.

f) Brief Summary of Plans for Work in Remaining Contract Period

In the remaining period of this contract, further optimization of the reaction schemes developed to date will be attempted for purposes of making the ceramer materials more efficiently and with controllable properties. Part of the effort will be directed towards the use of microwave processing of these systems since our more recent work has indicated that this method is a viable one to more rapidly cure these materials in much shorter time scales. Efforts will be made to investigate the adhesion behavior of the ceramer systems on substrates that include both inorganic as well as organic materials. Some work will also be initiated to investigate similar coating materials that are based on lower molecular weight functionalized organics, i.e., functionalized flexible spacers that will therefore allow a higher content of inorganic to be incorporated which may help enhance abrasion and wear properties of such systems over and above our present ceramers which tend to have a dominant composition of the functionalized oligomeric component. Finally, further work focusing on better understanding the level of extent and nature of the sol-gel reaction will continue utilizing solid state NMR as a means of characterizing a number of these systems - this work being carried out in conjunction with Dr. Charles Bronniman located at Colorado Sate University at Fort Collins, Colorado.

g) Name of Graduate Students/Post Doctoral Fellows Currently on the Project

Graduate Students: Anthony Brennan, David Rodrigues, Chinmay Betrabet

Post Doctoral Fellows: Bing Wang

PART III

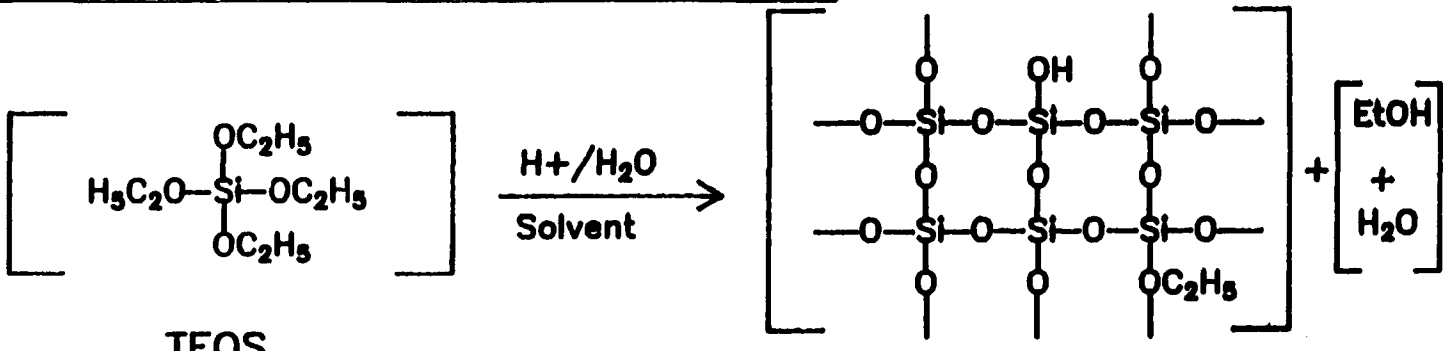
Explanatory Paragraph for Part III

Figure 1 provides a viewgraph of the general reaction scheme that will lead to the promotion of inorganic/organic hybrid networks known as ceramers through the use of sol gel chemistry. Viewgraph 2 illustrates the general morphological model of a ceramer based on polytetramethylene oxide (PTMO) and the metal alkoxide tetraorthosilicate (TEOS). This model illustrates that there are regions richer in the inorganic phase relative to the matrix component which is more dominated by the PTMO oligomers. The model also illustrates some degree of mixing of the silicate components with that of the PTMO. The origin of this model is based on extensive mechanical property testing as well as extensive small angle x-ray scattering studies of the prepared ceramer materials. One should recognize that the specific drawing shown in viewgraph 2 is of a more general nature and many other metal alkoxides and different organic oligomers could be substituted accordingly. Viewgraph 3 illustrates a plot of the sodium line refractive index versus the content of titanium that is utilized in preparing two different ceramer systems. The two ceramers utilize polytetramethylene oxide (PTMO) or, polyarylene ether sulfone (PSF) in the sol gel process to make these two different hybrid ceramers. One notes that the refractive index is linear with titanium content and shows values, at least in the case of the PSF ceramer, that reach somewhat above 1.75. Since organic polymers generally do not exceed much over the value 1.60, these new materials, which display some flexibility, indicate their potential for optical coatings by combining this novel approach utilizing organic sol gel metal alkoxide chemistry with that of functionalized organic oligomers to coreact into hybrid networks.

(Viewgraph 1)

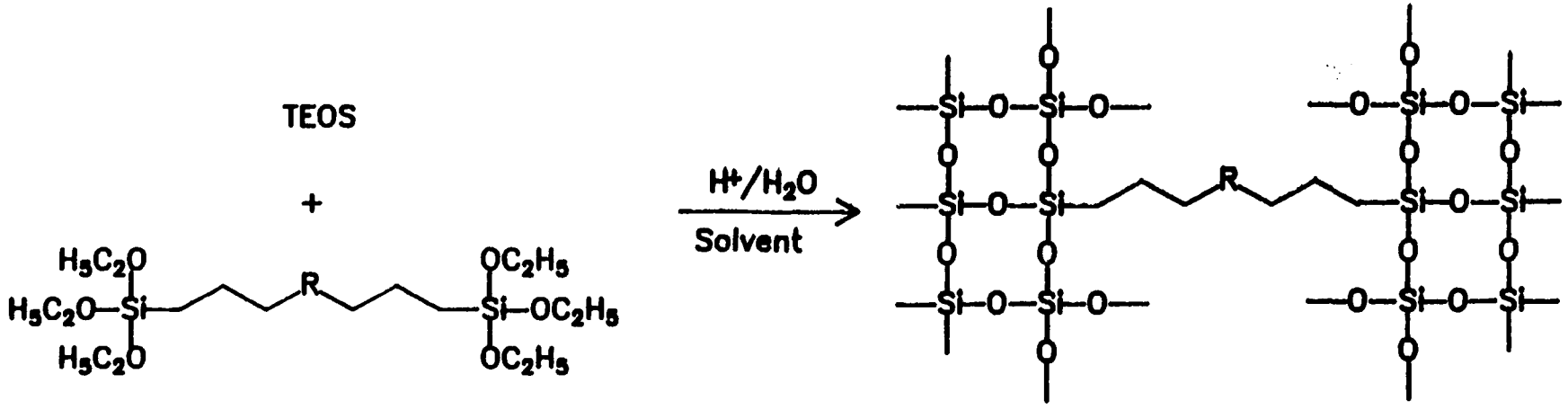
REACTION SCHEME FOR SYNTHESIS OF CERAMER – HYBRID

HYDROLYSIS/CONDENSATION OF METAL ALKOXIDES



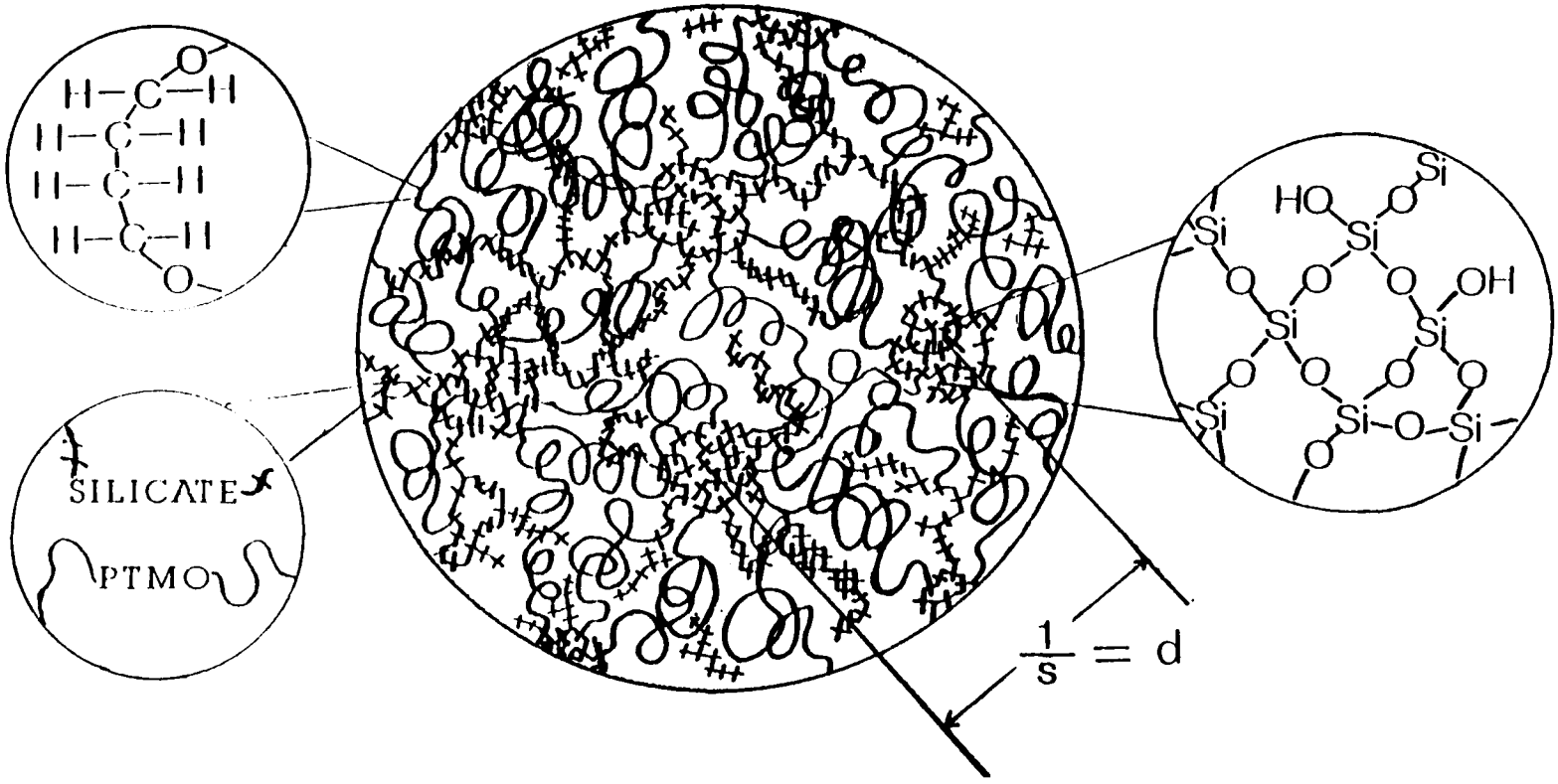
TEOS

INCORPORATION OF FUNCTIONALIZED OLIGOMERS INTO CERAMER



R = VARIOUS OLIGOMERS

(Viewgraph 2)



(Viewgraph 3)

Refractive Index, n_D (sodium line) of transparent titanium bond ceramers with functionalized polytetramethylene oxide (PTMO) or Polyarylene ether sulfone(PSF). The refractive index is shown as a function of the level of titanium content incorporated